



Dual fuel type solid oxide fuel cell using dimethyl ether and liquefied petroleum gas as fuels

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HIGHLIGHTS

- Steam reforming and evaluation of an SOFC fueled by DME and propane were carried out.
- DME was easily converted to reformat gas even at low S/C conditions.
- SOFC obtained similar performance when either DME or propane reformat gas was used.

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ABSTRACT

To clarify the potential of dimethyl ether (DME) as a fuel for solid oxide fuel cell (SOFC) systems designed for liquefied petroleum gas (LPG), steam reforming and evaluation of an SOFC fueled by DME and propane, a main component of LPG, were carried out.

Steam reforming of DME was tested over a commercial reforming catalyst, which easily converted DME to reformat gas with equilibrium gas composition. No carbon deposition over the catalyst's surface was observed at steam-carbon (S/C) ratio of 1.5. In addition, propane was easily reformed under steam reforming conditions at S/C 3.5. These results indicate that both DME and LPG are reformed well over the same catalyst and reformer. Evaluation of the SOFC performance was carried out by supplying reformat gases with equilibrium composition to an anode-supported small tubular cell. The SOFC obtained similar performance when either DME (S/C 2.0) or propane reformat gas (S/C 3.5) was supplied to the cell. In addition, when evaluation of cell performance was carried out under steady power, about the same level of DC electrical efficiency was realized when either DME (S/C 1.5) or propane reformat gas (S/C 3.5) was used.

The results show that DME can be used as a fuel for an SOFC system designed for LPG without drastic alterations to the system. In addition, DME and propane realize the same levels of power and power generating efficiency when the fuels are reformed at adequate S/C values.

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1. Introduction

In recent years, non-petroleum alternative fuels have become attractive because of concern over the depletion of petroleum resources and to suppress CO₂ emission. Dimethyl ether (DME) is a synthetic fuel that is produced from H₂ and CO. Because H₂ and CO are producible from many different sources (e.g., natural gas, biomass, coke, and waste), DME is seen as a promising alternative fuel candidate [1]. In particular, DME produced from biomass is carbon-neutral and has a great advantage for the reduction of CO₂ emission [2].

At the present time, there are very few devices that can use DME directly. Thus, for the diffuse of DME to spread as an alternative fuel, devices that can be fueled by DME must exist. In terms of time and economic considerations, it would be challenging to develop and diffuse devices specially designed for DME. Therefore the use of DME in devices that are designed for liquefied petroleum gas (LPG), which has properties similar to DME (e.g., boiling point and vapor pressure) [3], is being discussed. However, there are some properties that differ between DME and LPG, such as lubricity and swelling. If DME is to be used in conventional turbines or engines, these devices must be drastically changed and improved.

A solid oxide fuel cell (SOFC) is a power generating system that has beneficial effects on energy conservation and the suppression of CO₂ emission [4,5]. In Japan, more than 200 SOFC units for domestic use that are supplied with town gas, LPG, or kerosene

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have demonstrated their performance under practical conditions, and these systems are introduced to the market as of late [6].

In an SOFC system, fuels are often converted to a reformat gas mixture at a reformer before being supplied to the SOFC stacks. Therefore, if an SOFC system could reform DME in the same way as LPG and various parameters could be controlled to obtain the same level of power output despite changing the fuel supply, DME would be able to be used as a fuel for an SOFC system designed for LPG without drastically altering the system. However, at present, there exists no SOFC system that can use various types of fuels and there are few studies that have compared the power generation properties of SOFC when LPG and DME are used in same system.

To develop an SOFC system that is able to use both DME and LPG without substantial changes, we studied influence of the different fuels on SOFC performance. First, we carried out equilibrium calculation to estimate the reaction conditions for avoiding carbon deposition and carried out steam reforming of DME and propane, a major component of LPG, over a commercial catalyst to compare the reaction conditions required to reform the fuels successfully without carbon deposition. In addition, we generated simulated reformat gases by a novel method we developed and then supplied these reformates to a tubular-anode-supported SOFC to evaluate effect of different fuels on the cell performance.

2. Experimental

2.1. Steam reforming of DME and propane

Influence of the reaction temperature and the steam-carbon (S/C) ratio in the reaction mixture upon carbon deposition was estimated by thermodynamic equilibrium calculations [7,8] that were carried out with the help of a computer program [9]. These results were used as references for defining the reaction conditions of the steam reforming.

Steam reforming of DME and propane was conducted in a fixed-bed tubular Inconel reactor. 2 mL (2.19 g) of commercial Ni/Al₂O₃ catalyst (FCR-4, Süd-Chemie Catalysts) was loaded into the reactor and was reduced at 700 °C for 1 h under a flowing H₂/N₂ mixture, H₂/N₂ = 40/160 standard cubic centimeter per minute (sccm, reference conditions: 0 °C, 101.3 kPa). After the reduction fuel-steam mixture was supplied to the catalyst bed. The test was started at 550 °C, and catalyst bed was heated up to 700 °C in increments of 50 °C with an electrical muffle furnace. Catalyst bed was kept for 1 h at each temperature. DME and propane were supplied to the catalyst bed under atmospheric pressure with a thermal mass-flow controller (FC-7800C, Advanced Energy), and steam was generated by vaporization of water by a vaporizer and HPLC pump (LC-10AT, Shimadzu). Mass-flow rates of the DME and propane were set to 20.0 and 30.8 sccm, respectively. The reaction products were also analyzed by using a micro-gas chromatograph equipped with thermal conductivity detectors (CP-4900, VARIAN) after the water vapor included in reaction mixture was removed by a cold trap.

After steam reforming, deposited carbon was quantified by a temperature-programmed oxidation method (TPO). After the reaction, the catalyst was heated to 1000 °C at a rate of 10 °C min⁻¹ in an O₂/Ar mixture (1/19, 30 sccm). CO_x gases derived from deposited carbon were passed through a methanator and then methane concentration was monitored with a flame ionization detector (FID).

2.2. Generation of simulated reformat gas

We previously reported on the development of a simulated-reformat-gas generator [10,11]. The generator produces

simulated reformat gases easily and safely because only H₂, O₂, and CO₂ are used as reactant gases and toxic CO is not directly used. This generator consists of a catalytic H₂ combustor (H₂ + 0.5O₂ = H₂O), in which an H₂–H₂O gas mixture can be stably generated, and a catalytic equilibrium reactor, in which equilibrium compositions during steam reforming are synthesized via reverse water gas shift reactions (CO₂ + H₂ = CO + H₂O) and methanation reactions (CO₂ + 4H₂ = CH₄ + 2H₂O). The generator we developed can supply simulated reformat gas to the anode side at various compositions and flow rates with high precision. Therefore we can easily carry out evaluations of SOFC performance.

Fig. 1 shows a schematic diagram of the simulated-reformat-gas generator. The generator consists of three thermal mass-flow controllers, a catalytic H₂ combustor, and a catalytic equilibrium reactor. The flow rates of H₂, O₂, and CO₂ are controlled to coincide with the C–H–O ratio of the steam reformat gases to simulate.

2.3. Fabrication and evaluation of the SOFC

To fabricate an anode-supported-tubular SOFC, first an NiO-(Y₂O₃)_{0.08}(ZrO₂)_{0.92} (NiO 60 wt%) porous tube is formed by a cold isostatic pressing method. After calcining the support tube, the NiO-(Y₂O₃)_{0.08}(ZrO₂)_{0.92} anode, Zr_{0.89}Sc_{0.1}Ce_{0.01}O_{1.95} electrolyte, (Ce_{0.9}Gd_{0.1})O₂ interlayer, and (Sm_{0.5}Sr_{0.5})CoO₃ cathode are fabricated by a slurry coating method and sintered in turn. Details regarding the cell fabrication process are reported in our previous study [12]. The interlayer is used to prevent a reaction between the electrolyte and cathode. The length, outer diameter, and effective electrode area (cathode) of the cell are 65 mm, 13 mm, and 26 cm², respectively. Silver meshes are used for current collection of the cathode.

To evaluate the power generation properties of the cell, the cell was connected to a stainless support tube and placed in an electric furnace (Fig. 1). Simulated reformat gases of DME and propane were generated in the simulated gas generator described above and were fed to the anode as fuels. An O₂–N₂ mixture (O₂/N₂ = 1/4), which mimicked the air, was supplied as the cathode gas. Experimental pipelines were placed in an oven and heated above 150 °C

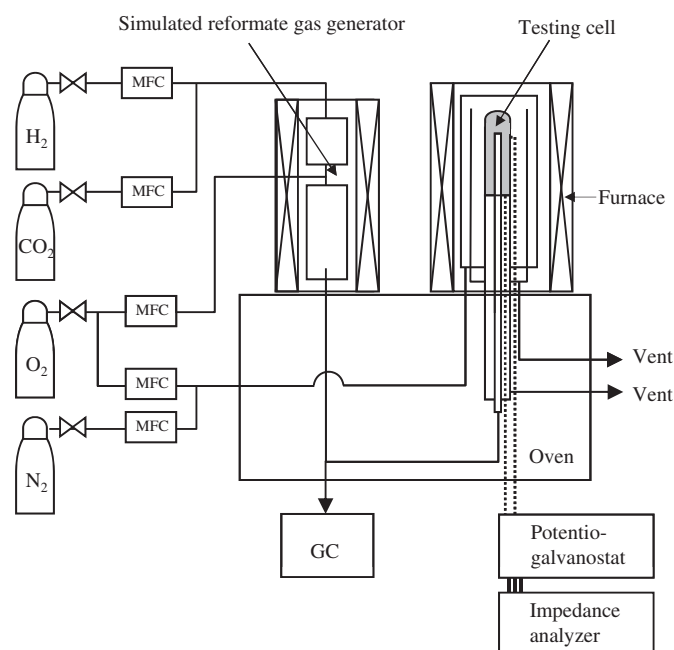


Fig. 1. Schematic diagram of the cell evaluation system and model gas generator.

to avoid the condensation of steam to water. The cell evaluation was operated at 750 °C. The electrochemical cell performance was estimated by current density–voltage measurements by using a potentio-galvanostat (HZ-5000, HOKUTO DENKO).

3. Results and discussion

3.1. Steam reforming of DME and propane

The ratios between DME or propane and steam required to avoid carbon deposition were estimated by thermodynamic equilibrium calculations (Fig. 2). The results show that carbon deposition occurs easily at around 550 °C for both fuels. When steam reforming is carried out above 500 °C, a large amount of steam above S/C 1.8 is required to be supplied to avoid carbon deposition in the case of propane. On the other hand, in the case of DME, the potential conditions that induce carbon deposition are limited compared with propane and about S/C 1.5 is needed to avoid carbon deposition. In actuality, however, when propane is used as a fuel, an excess amount of steam (S/C > 3.0) are required [13] to suppress carbon deposition in spite of the results of the equilibrium calculations because propane has a C–C bond in its molecular structure. On the other hand, DME does not have a C–C bond and the risk of carbon deposition is lower than for propane. Thus we carried out steam reforming of DME and propane over a commercial Ni/Al₂O₃ catalyst to verify that that DME is able to reform under low S/C conditions.

Fig. 3 shows the dry gas compositions of the effluent gases at different temperatures. The broken lines show the dry gas compositions of the reformat gases in the equilibrium state.

When propane steam reforming was carried out at S/C 3.5, almost all the propane was consumed above 550 °C. There was a difference in gas composition from equilibrium values of up to ±4% at about 550–600 °C. However, above 700 °C the gas compositions conformed well to the equilibrium values within ±1%. After a steam reforming test, no carbon deposition was observed over the catalyst's surface because amount of the carbon was below detection limit of TPO. When steam reforming was carried out at S/C 3.0, carbon deposition clearly occurred after the reaction. Especially above 3 wt% of carbon was deposited over the catalyst at outlet of the bed. The results show that greater than S/C 3.5 is essential to suppress carbon deposition and that fuel can be reformed stably for a long time in propane steam reforming.

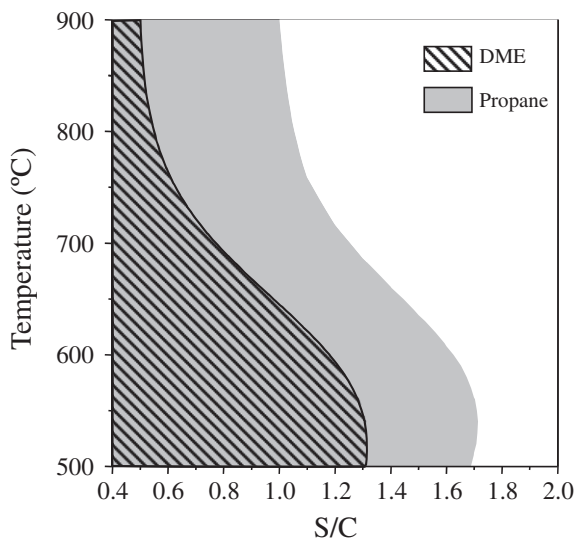


Fig. 2. Thermodynamic carbon deposition domain of propane and of DME in steam reforming.

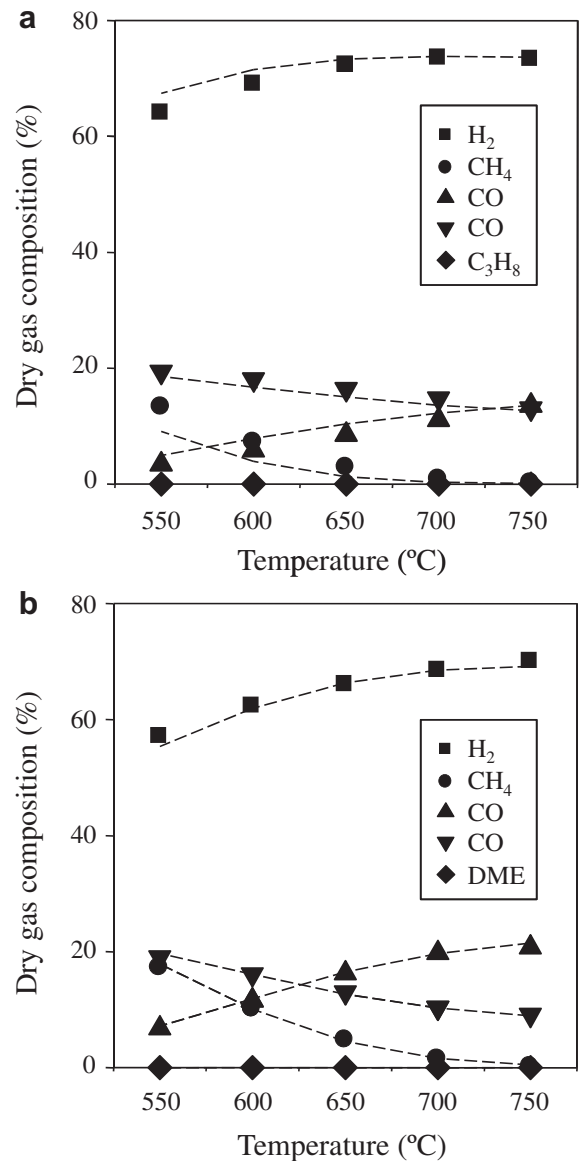


Fig. 3. Dry gas compositions of reformat gases. (a) Propane at S/C 3.5, (b) DME at S/C 1.5.

Subsequent DME steam reforming was performed at S/C 1.5. As a result, DME was also completely consumed at around 550–750 °C. The dry gas compositions conformed well to the equilibrium values within ±2% despite the 500 °C temperature and the formation of C₂–C₃ byproducts was not observed. In addition, carbon deposition over the catalyst's surface was not observed. Laosiripojana et al. reported that DME was decomposed above 825 °C in homogeneous (non-catalytic) steam reforming [14]. This decomposition has the potential of carbon deposition at the part maintained high temperature in the SOFC system, e.g. pipe, inlet of the reformer, and cell-stack. Therefore adequate measures are very important in order to the using DME for the SOFC.

The above results clearly show that it is possible to reform two different fuels over the same catalyst and suppress carbon deposition by supplying the appropriate amount of steam. This indicates that a reformer for propane that is equipped in an SOFC system could be applied to the reforming of DME.

Table 1
Dry gas compositions of simulated reformat gases at 650 °C and equilibrium values.

Fuel		S/C	Dry gas composition (%)				
			H ₂	CH ₄	CO	CO ₂	Fuel
DME	Simulated gas	1.5	66.2	4.1	16.9	12.9	0
		2.0	68.7	2.4	14.2	14.7	0
		3.0	71.9	0.9	9.7	17.6	0
	Equilibrium	1.5	66.4	4.5	16.5	12.7	0
		2.0	68.8	2.7	14.1	14.4	0
		3.0	71.2	1.1	10.8	16.9	0
Propane	Simulated gas	3.5	74.1	1.1	9.2	15.6	0
	Equilibrium	3.5	73.4	1.3	10.4	15.0	0

3.2. Influence of S/C on SOFC performance

Evaluation of SOFC performance was carried out by supplying reformat gases. The evaluation conditions were based on the results of Section 3.1. Simulated reformat gases obtained from the generator described in Section 2.2 were used to simplify the evaluation process. Before the SOFC evaluation, as a preliminary test, simulated reformat gases were generated at different conditions and compared to equilibrium values. The results are summarized in Table 1. In spite of the conditions, the gas composition of the simulated reformat gases agreed well with equilibrium gas composition within ± 1 mol%. The following evaluation of the SOFC performance was carried out by using simulated reformat gases, all of which were supplied by the generator described above.

Fig. 4 shows the relationships between current and cell voltage (I – V curve) and current and power (I – P curve). The supplied simulated reformat gas mimicked DME reformat at S/C 1.5, 2.0, and 3.0 and propane reformat at S/C 3.5. The flow rate of the reformat gas was kept constant during the evaluation, simulated flow rate of propane and DME are 3.0 sccm and 4.6 sccm, respectively. As the result, the lower heating values (LHV) per minute of propane and DME were also held constant (-274 J min^{-1}).

When DME reformat gas was supplied to the cell, the open circuit voltage (OCV) increased with decreases in the assumed S/C. The OCV observed when supplying the DME reformat gas at S/C 1.5 was 27 mV higher than at S/C 3.0. In addition, the maximum cell voltage was obtained by supplying DME reformat gas at S/C 1.5

regardless of the value of the current. The OCVs obtained when supplying propane (S/C 3.5) and DME simulated reformat gas (S/C 3.0) were approximately the same. Therefore, it can be said that DME realized a higher cell voltage compared with propane reformed at S/C 3.5, if the DME was reformed at S/C below 3.0. However, the slopes of the I – V curves obtained when supplying DME are steeper than those obtained from propane. The cell voltage obtained from supplying propane (S/C 3.5) came close to that obtained from DME (S/C 2.0).

Output powers of the cell at $I = 3 \text{ A}$ when supplied with different simulated reformat gases were compared (Fig. 5). The order of the obtained cell power was as follows: DME (S/C 1.5) > propane (S/C 3.5) \approx DME (S/C 2.0) > DME (S/C 3.0). The maximum power, 2.07 W, was obtained when supplying DME reformat gas (S/C 1.5). In the evaluation, all of the reformat gases were generated under the condition that the original fuels had the same LHV per minute. Thus maximum power efficiency was obtained when the cell was supplied with DME reformat gas (S/C 1.5).

We have shown that under the conditions that the original supplied fuels had the same amount of LHV per minute and the total flow rate of the reformat gas was kept constant, a cell supplied with DME reformat gas reformed below S/C 2.0 realized equal or higher power and electrical efficiency.

3.3. Comparison of SOFC performance under constant fuel utilization

To investigate influence of different fuels on SOFC performance under constant fuel utilization (U_f) [11]. In this paper, U_f is defined with a current drawn to outer circuit, or I and a theoretical current at 100% utilization of a fuel, I_{theory} as follows:

$$U_f = I/I_{\text{theory}} = I/(nFm_{\text{fuel}}) \quad (1)$$

where n : number of electron transferred in electrochemical oxidation of a fuel molecule, F : Faraday's constant, m_{fuel} : molar flow rate of a fuel. We determined and compared V – I plots at $U_f = 70\%$ (Fig. 6). At each value of the current, DME reformat gas (S/C 1.5) yielded 16–26 mV higher cell voltage compared with the case of propane reformat gas (S/C 3.5) in the range we studied. In addition, the voltage difference between the two reformat gases expanded with increased current.

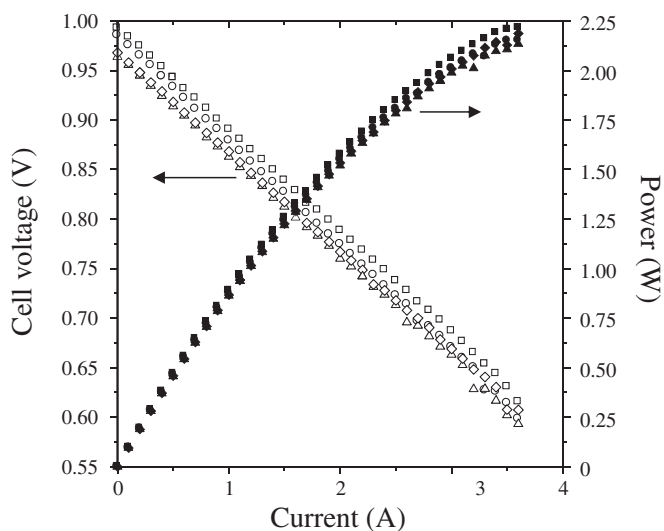


Fig. 4. I – V (open) and I – P (closed) plots for the cell evaluation at 750 °C with constant fuel flow under different S/C conditions. (\square) DME S/C 1.5, (\circ) DME S/C 2.0, (\triangle) DME S/C 3.0, (\diamond) propane S/C 3.5.

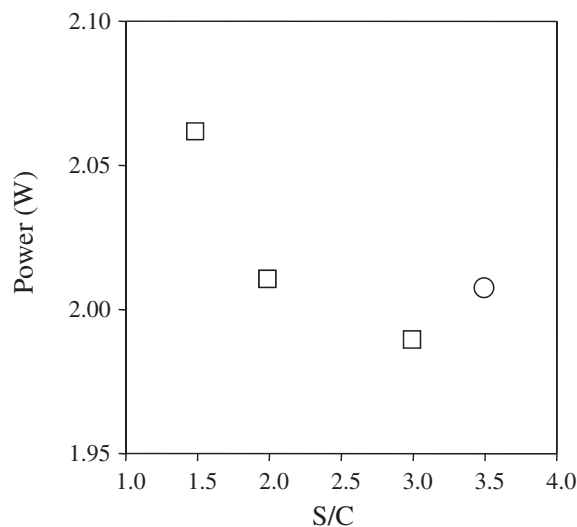


Fig. 5. Effect of S/C on power generation of the SOFC at 3 A and 750 °C. (\square) DME, (\circ) propane.

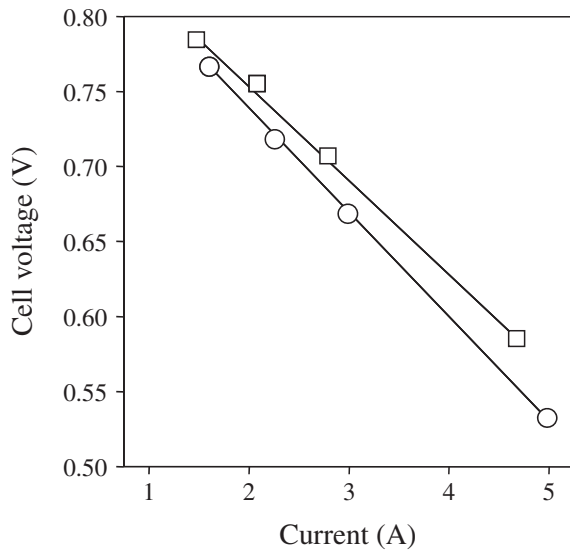


Fig. 6. I – V plots for cell evaluation at 750 °C and $U_f = 70\%$. (□) DME, (○) propane.

Next, we compared power and DC electrical efficiency (η_{DC}) by using the results shown in Fig. 6. The values of η_{DC} were obtained from

$$\eta_{DC} = V / (-\Delta H / nF) \times U_f \quad (2)$$

where V is cell voltage, ΔH is the lower heat value of the fuel at 25 °C and 101.3 kPa.

Fig. 7 displays the I – P and I – η_{DC} plots. DME reformat gas (S/C 1.5) yielded a higher power value than propane reformat gas (S/C 3.5) at the same value of the current. In addition, the figure clearly shows how to obtain the same level of output between propane and DME under constant U_f . When DME is supplied, the sweep current and fuel supply should be decreased in comparison to propane.

When the same values of power = 2.3 W was obtained from both of the reformat gases, propane and DME could obtain equal values of η_{DC} (39.8%, broken line in Fig. 7). Above 2.3 W, however, DME yielded a higher value of η_{DC} than propane (e.g. dotted line in Fig. 7). In Table 2, values of n , ΔH , and $-\Delta H/nF$ of both DME and propane are summarized. The values of η_{DC} can be obtained by

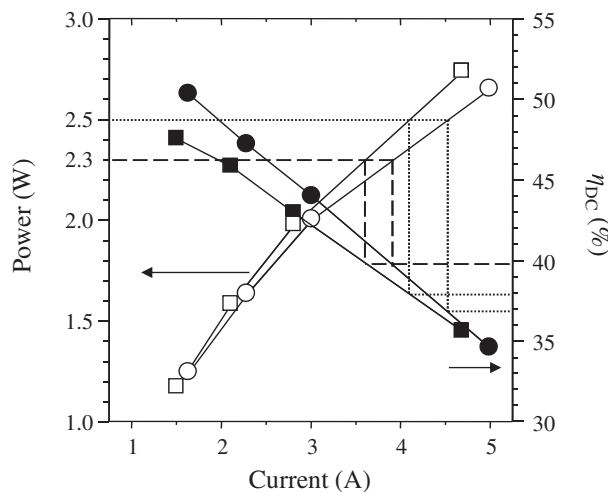


Fig. 7. I – P (open) and I – η_{DC} (closed) plots for cell evaluation at 750 °C and $U_f = 70\%$. (□) DME, (○) propane.

Table 2

Thermodynamic parameters of DME and propane.

	ΔH (kJ mol ⁻¹)	n	$-\Delta H/nF$ (V)
DME	-1328	12	1.15
Propane	-2044	20	1.06

using Eq. (2). The value of $-\Delta H/nF$ for DME is 10% higher than that of propane because n for DME is less than for propane. Therefore, even if both DME and propane reformates obtained the same cell voltages, propane would show higher η_{DC} than would DME. Thus one could say that DME is a less efficient fuel. However, as is shown in Fig. 7, at constant U_f , DME reformat obtained a higher cell voltage than did propane and the difference between the cell voltages of the two reformates increased with increasing current. Therefore, DME obtained a higher η_{DC} than propane reformat in the range where an SOFC has a large output. This indicates that DME can be an efficient fuel for SOFC systems under limited conditions.

4. Conclusions

To clarify the feasibility of a dual-fuel type SOFC that uses DME and LPG as fuels, we carried out catalytic reforming of the fuels and evaluated SOFC performance. Our results are summarized as follows.

- DME and propane steam reforming over a commercial catalyst (Ni/Al₂O₃) was carried out. The results of equilibrium calculations suggested that it is possible to avoid carbon deposition at the conditions of S/C 1.8 for propane and S/C 1.5 for DME. However, in actual experience, above S/C 3.5 propane steam reforming required an excessive amount of steam to inhibit carbon deposition. On the other hand, DME steam reforming could be carried out at S/C 1.5 to obtain reformat gas with equilibrium gas composition.
- Cell performance was evaluated by flowing reformat gases that mimicked different values of S/C and had the same constant LHV per minute of the original fuels. DME reformat gas reformed below S/C 2.0 could obtain the same or higher cell voltage and output compared with that of propane reformat gas (S/C 3.5).
- SOFC performance was evaluated under constant U_f and supplied with DME (S/C 1.5) or propane (S/C 3.5) reformat gas. At $U_f = 70\%$, DME showed higher cell voltage and power than with propane. In addition, when power was above 2.3 W, DME displayed higher power generation efficiency than propane.

These results suggest that 1) a reformer designed for propane can be used for DME steam reforming, and 2) even if the fuel is switched from propane to DME, comparable electrical efficiency and power can be obtained by regulating the flow rates of fuel and steam. Therefore, if appropriate measures are taken for SOFCs to avoid problems such as the corrosion of rubber seals and control of the reformer temperature, dual fuel type SOFCs that are fueled by LPG and DME can be realized.

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